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The Nucleophilic Photo-substitution Reaction of Anthraquinone Derivatives. II. The Mechanism of the Photoamination of Sodium 1-Amino-4-bromoanthraquinone-2-sulfonate

Haruo Inoue, Kenichi Nakamura, Seijiro Katô, and Mitsuhiko Hida
Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158

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The photoamination of sodium 1-amino-4-bromoanthraquinone-2-sulfonate (I) by ammonia or alkylamines in aerated 4 : 1 2-propanol-water was investigated. No effect on the reaction was observed by the addition of Rose Bengal as the addition of the triplet quenchers. The reciprocal of the quantum yield was proportional to the reciprocals of both the partial pressure of oxygen and the concentration of the amine. The peroxide was produced as the photoamination proceeded, and the simultaneous photodecomposition took place in a constant ratio to the photoamination. This reaction scheme for the photoamination of (I) was proposed: the exciplex was formed by the excited (I) (^{1}CT) and the ground-state oxygen, followed by the nucleophilic attack of the amine.

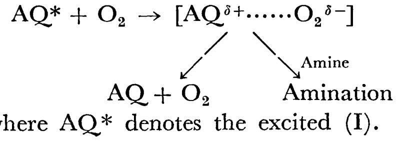
While many detailed studies have been made of the photochemical behavior of anthraquinone derivatives, especially the photoreduction by a hydrogen abstraction reaction in their excited $n\pi^*$ triplet states, few examples of the photosubstitution reaction of anthraquinones have been known.1,2) However, recently many reports have been written on the photochlorination, the photoamination, and the photohydroxylation of anthraquinone derivatives.3–15) Richards and his co-workers proposed an interesting reaction scheme for the photohydroxylation of 1-methoxyanthraquinone in which the reaction product was formed by the attack of a hydroxyl ion on the photochemically generated semiquinone radical anion. We also have found that the bromine atom of sodium 1-amino-4-bromoanthraquinone-2-sulfonate (I) is replaced by ammonia or alkylamines under the irradiation of visible light.16) In a previous paper we reported that: 1) the presence of the oxygen molecule is essential for the photoamination of (I); 2) the effect of the addition of the oxidizer suggests that the dissolved oxygen does not act as a smiple oxidizing agent, but plays a more complicated role in the photoamination; 3) any reaction scheme including the photoreduction of (I) can be excluded; 4) the reaction is induced by the absorption of the light corresponding to the first absorption band of (I), and 5) the solvent effect suggests the presence of a polar intermediate in the reaction.17) On taking account of the role of oxygen in the photoamination of (I), the following several reaction schemes are possible.

Scheme A: The oxygen molecule participates in the photoamination as a singlet oxygen.

Scheme B: The photoamination of (I) proceeds through some interaction between the excited (I) and the ground-state oxygen as follows.

a) The oxygen enhances the intersystem crossing between the lowest excited singlet and triplet states of (I). The latter state is assumed to be active in the photoamination

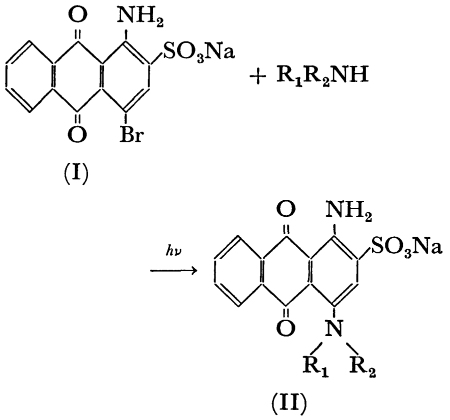
b) The photoamination proceeds through the exciplex between the excited (I) and the ground-state oxygen, such as:



$$\mathrm{AQ}^* + \mathrm{O}_2 \rightarrow [\mathrm{AQ}^{\delta+}\cdots\cdots\mathrm{O}_2{}^{\delta-}] \begin{cases} \swarrow\ \mathrm{AQ} + \mathrm{O}_2 \\ \searrow^{\mathrm{Amine}}\ \mathrm{Amination} \end{cases}$$

where AQ* denotes the excited (I).

In the present paper we will report the results obtained by photochemical studies of the photoamination of (I) and propose that the best reaction scheme is Scheme B-b), including the exciplex formation between (I) in its excited singlet state and the ground-state oxygen.



Experimental

The sodium 1-amino-4-bromoanthraquinone-2-sulfonate (I) and 2-propanol were purified as has been reported previously.17) Shimadzu UV-200 spectrophotometer was used for the measurement of the visible and UV spectra. The quantum yield of the photoamination of (I) was determined by the use of a potassium ferrioxalate chemical actinometer according to the method recommended by Hatchard and Parker.18) A quantitative analysis of the peroxide produced in the reaction system was carried out by the colorimetric iodide method.19) The reaction mixture was irradiated by meas of a 500 W xenone lamp (USHIO UXL-500DXO) or a 100 W high-pressure mercury lamp (Eikosha) through the following filter system: a Toshiba interference filter KL-47 and a glass filter VY-45 were used for the monochromatic light (λ=468 nm) irradiation, soda glass for the irradiation of $\lambda>300$ nm, and a Toshiba glass filter VO-57 for the irradiation for $\lambda>550$ nm.

Results and Discussion

Effect of the Oxygen. If the singlet oxygen participates in the reaction of the photoamination of (I), a promotive effect can be expected upon the addition of Rose Bengal as a singlet oxygen sensitizer. Solutions of (I) (1.000×10^{-4} mol/l) and ammonia

TABLE 1. EFFECT OF THE ADDITION OF ROSE BENGAL ON THE PHOTOAMINATION OF (I) BY AMMONIA

[Rose Bengal] (mol/l)	Yield of the aminated product (%)[a]
0	31.0
5×10^{-6}	21.5

a) 15 min irradiation of $\lambda > 300$ nm by Xe 500 W lamp.

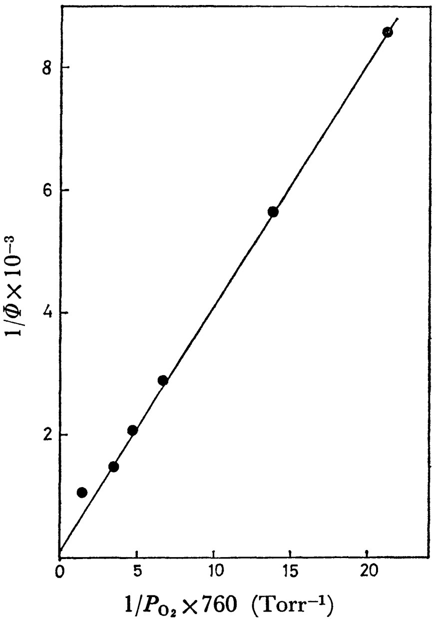


Fig. 1. Effect of the partial pressure of the oxygen on the quantum yield Φ of the photoamination of (I). $[I]\sim1.00\times10^{-4}$ mol/l, $[NH_3]\sim5.00\times10^{-2}$ mol/l in 4 : 1 2-propanol-water, irradiation of $\lambda=468$ nm.

$(5.00\times10^{-2}$ mol/l) in aerated 4 : 1 2-propanol–water with and without Rose Bengal $(5.00\times10^{-6}$ mol/l) were irradiated by the light of $\lambda > 300$ nm or $\lambda > 550$ nm. In the case of the irradiation of $\lambda > 300$ nm, which excites both (I) and Rose Bengal, no promotive effect was observed upon the addition of Rose Bengal. The retardative results shown in Table 1 can be attributed to the inner-filter effect of Rose Bengal. Moreover, no amination was observed upon the irradiation of $\lambda > 550$ nm, which excites only Rose Bengal. These results probably exclude the reaction scheme including the singlet-oxygen formation. Consequently, the other reaction scheme, including the interaction between the excited (I) and the ground-state oxygen, is probable. As is shown in Fig. 1, a plot of the reciprocal of the quantum yield of the photoamination of (I) *vs.* the reciprocal of the partial pressure of the oxygen in the reaction cell gave a good straight line. This strongly suggests that the photoamination proceeds through the collision process between the oxygen molecule and a transient intermediate such as the excited (I).

Formation of the Peroxide. The addition of acetic acid and a 20% aqueous solution of potassium iodide to the irradiated reaction mixture of (I) $(1.00\times10^{-4}$ mol/l) and ammonia $(5.00\times10^{-2}$ mol/l) in aerated 2-propanol–water increased the absorption intensity at 357 nm. The enhancement of the absorption intensity at 357 nm, which is characteristic of the triiodide ion, I_3^-, shows the formation of peroxide. Hence, the amount of peroxide produced in the reaction system was estimated by means of the difference in the absorption intensity at 357 nm between the irradiated and the unirradiated solutions, because the absorption intensity of the unirradiated reaction mixture is unchanged by the addition of acetic acid and a potassium iodide aqueous solution.[20] As is shown in Table 2, the peroxide was produced as the photoamination of (I) proceeded. When ammonia was absent, no photoamination could occur and the peroxide was not produced at all. These results indicate that the peroxide is formed in the course of the photoamination of (I). When alkylamines were used in place of ammonia, the peroxide was also produced in the same manner. The amounts of the peroxide produced in the reaction system in the case of various amines at nearly the same conversion of (I) are compared in Table 3. If a formation of the exciplex such as $[AQ^{\delta+}\cdots O_2^{\delta-}]$ is assumed in the photoamination, it seems reasonable that the super oxide ion O_2^- and, consequently, the peroxide are produced as the reaction proceeds.

TABLE 2. PEROXIDE FORMATION DURING THE PHOTOAMINATION

$([I]\sim1.00\times10^{-4}$ mol/l in 4 : 1 aerated 2-propanol-water)

Irradiation time[a] (min)	NH_3 (mol/l)	Yield of the aminated product (mol/l)	Peroxide in the reaction system (mol/l)
0	5.00×10^{-2}	0	0
7	5.00×10^{-2}	10.6×10^{-6}	2.34×10^{-6}
13	5.00×10^{-2}	29.5	7.8
30	5.00×10^{-2}	48.3	10.6
20	0	0	0

a) Irradiation of $\lambda > 300$ nm by Xe 500 W lamp.

TABLE 3. PEROXIDE FORMATION IN THE CASE OF VARIOUS AMINES

Amine	NH_3	CH_3NH_2	$C_2H_5NH_2$	n-$C_4H_9NH_2$
[Peroxide]$\times10^6$ (mol/l)	10.6	132	138	166
Conversion of I (%)	48.3	43.6	43.5	43.0

Effect of the Triplet Quencher. In order to clarify the multiplicity of the reactive excited state in the photoamination, the effect of the triplet quenchers on the reaction was studied. The solution of (I) $(1.00\times10^{-4}$ mol/l) and ammonia $(5.00\times10^{-2}$ mol/l) in aerated 4 : 1 2-propanol–water with or without a triplet quencher (*ca.* 10^{-2}—10^{-4} mol/l) such as naphthalene $(E_T=60.9$ kcal/mol), anthracene $(E_T=42.0$ kcal/mol), or naphthacene $(E_T=29.3$ kcal/mol), was irradiated by the monochromatic light of $\lambda=468$ nm which excites only (I). In no case was any quenching effect observed. Since it has been reported that anthraquinones have their $n\pi^*$ triplet states in *ca.* 62—3 kcal/mol and 1-aminoanthraquinone has

Table 4. The values of the ratio of the intercept to the gradient in the plot of $1/\Phi$ *vs.* 1/[amine] ([I]$\sim$1.00$\times$10^{-4} mol/l in aerated 4 : 1 2-propanol-water, irradiation of λ=468 nm by Xe 500 W lamp)

Amine	CH_3NH_2	$C_2H_5NH_2$	$C_6H_5CH_2NH_2$	NH_3	n-$C_4H_9NH_2$	$\underbrace{CH_2\text{-}(CH_2)_4\text{-}NH}$	$(n\text{-}C_4H_9)_2NH$
pK_a	10.62	10.63	9.34	9.21	10.43	11.22	11.25
$\frac{\text{Intercept}}{\text{Gradient}}$ (mol^{-1}·l)	89	72	75	68	51	43	42

its intramolecular CT triplet state between 47.1 kcal/mol and 42.1 kcal/mol[21], the above fact indicates that the excited singlet state of (I) is the active one in the photoamination. As has previously been reported, the amination is induced by the absorption of the light corresponding to the first absorption band, which inherently has an intramolecular CT nature. Thus, it may be concluded that the photoaminatuin of (I) proceeds through the lowest excited singlet CT state of (I) and that Scheme B-a), in which the lowest excited triplet state is the active one, can also be excluded.

Effect of the Concentration of the Amine. The effect of the concentration of the amine on the quantum yield of the photoamination was studied. A representative, good linear plot of the reciprocal of the concentration of ammonia against the reciprocal of the quantum yield is shown in Fig. 2. A similar relationship was also found in every alkylamine, such as methylamine, ethylamine, n-butylamine, benzylamine, di-n-butylamine, and piperidine. These results strongly suggest the presence of a collisional process between the amine and a transient intermediate in the course of the photoamination. The values of the intercept divided by the gradient in the plot of $1/\Phi$ *vs.* 1/[amine] and the value of pK_a of each amine are compared in Table 4.

Simultaneous Photodecomposition. As has been reported previously, the photoreaction of (I) with ammonia in an aerated 4 : 1 2-propanol–water mixture by the irradiation of the visible light gave only one colored product (II).[17] However, as is shown in Table 5, the conversion (%) of (I) was not equal to the yield (%) of (II) and the ratio of the yield to the conversion had an almost constant value of 0.62 during the course of the photoreaction,—that is, about 40% of the conversion of (I) was the yield of the other compound, which has no absorption band in the visible region. From the paper-chromatogram of the concentrated reaction mixture, a pale yellow, unknown compound was indeed isolated; it has no absorption band in the region of λ>400 nm. The pH measurement of the reaction system ([I]$\sim$1.00$\times$10^{-4} mol/l, [NH_3]$\sim$5.00$\times$10^{-2} mol/l in 4 : 1 2-propanol–water) indicated that the amount of OH^- did not exceed more than 1$\times$10^{-4} mol/l. When the amine was absent, (I) and the reaction product (II) alone did not decompose at all upon the irradiation of visible light and only a slight photodecomposition occurred in the presence of OH^- (1$\times$10^{-4} mol/l). Consequently, it may be concluded that the photoamination proceeds competitively with the photodecomposition of (I). Moreover, the fact that the ratio of the yield to the conversion has a constant value during the course of the photoamination strongly suggests that the photoamination and the simultaneous photodecomposition proceed through a common intermediate in a certain ratio. Similar phenomena

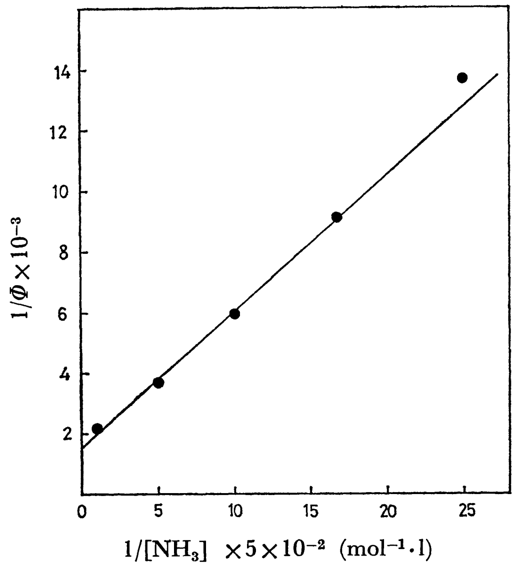


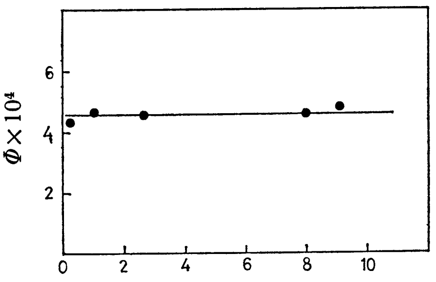
Fig. 2. Effect of the concentration of ammonia on the quantum yield Φ of the photoamination of (I). [I]$\sim$1.00$\times$10^{-4} mol/l in aerated 4 : 1 2-propanol-water, irradiation of λ=468 nm

Table 5. The conversion of (I) and the yield of (II) in the photoamination of (I) by ammonia
([I]$\sim$1.00$\times$10^{-4} mol/l, [NH_3]$\sim$5.00$\times$10^{-2} mol/l in aerated 4 : 1 2-propanol-water, irradiation of λ>300 nm by high pressure Hg lamp)

Irradiation time (h)	Conversion of I (%)	Yield of II (%)	$\frac{\text{Yield}}{\text{Conversion}}$
2	32.6	20.0	0.61
4	53.5	33.2	0.62
6	68.2	42.1	0.62
8	78.4	48.6	0.62

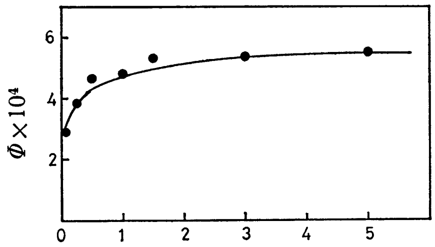
Table 6. The ratio of the yield of (II) to the conversion of (I) in the photoamination of (I) by various amines
([I]$\sim$1.00$\times$10^{-4} mol/l, [amine]$\sim$5.00$\times$10^{-2} mol/l in aerated 4 : 1 2-propanol-water)

Amine	NH_3	CH_3NH_2	$C_2H_5NH_2$	n-$C_4H_9NH_2$
$\frac{\text{Yield of (II)}}{\text{Conversion of (I)}}$	0.62	0.66	0.67	0.73



$\times 10^{15}$ quanta/s
Intensity of the incident light

Fig. 3. Effect of the intensity of the incident light on the quantum yield Φ of the photoamination of (I). $[\mathrm{I}] \sim 1.00 \times 10^{-4}$ mol/l, $[\mathrm{NH_3}] \sim 5.00 \times 10^{-2}$ mol/l in aerated 4 : 1 2-propanol-water, irradiation of $\lambda = 468$ nm.



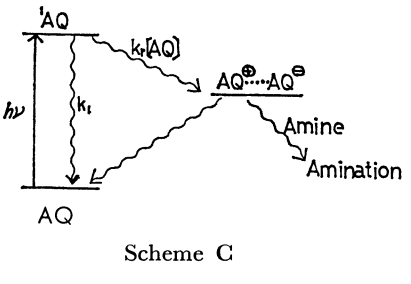
$[\mathrm{I}] \times 10^4$ (mol/l)

Fig. 4. Effect of the concentration of (I) on the quantum yield Φ of the photoamination of (I). $[\mathrm{NH_3}] \sim 5.00 \times 10^{-2}$ mol/l in aerated 4 : 1 2-propanol-water, irradiation of $\lambda = 468$ nm.

were also observed in other amines; the various ratios of the yield to the conversion in the amines are compared in Table 6.

Effect of the Intensity of the Incident Light. As is shown in Fig. 3, the quantum yield was constant, independent of the intensity of the incident light. This clearly indicates that the photoamination of (I) requires only one photon and that any reaction scheme which requires two photon is invalid.

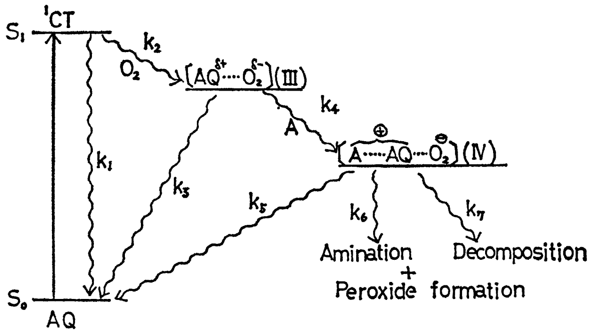
Effect of the Concentration of (I). Figure 4 shows that the quantum yield increased gradually with the increase in the concentration of (I). This suggests that the second molecule of (I) participates in the photoamination of (I). A linear relationship between $1/\Phi$ and $1/[\mathrm{I}]$ was approximately obtained; the ratio of the intercept to the gradient in the plot was estimated to be about $10^5\ \mathrm{mol^{-1} \cdot l}$. If the photoamination of (I) proceeds through the D-D scheme[22], which has been reported in the photofading of the xanthene dyes as Scheme C:



Scheme C

where k_1 denotes the deactivation rate constant of the excited (I) and k_r, the rate constant of the reaction between the excited (I) and the second (I), k_r/k_1 can be estimated as $10^5\ \mathrm{mol^{-1} \cdot l}$. As k_r is smaller than the diffusion-controlled rate constant ($10^{10}\ \mathrm{mol^{-1} \cdot l\ s^{-1}}$), k_1 should be smaller than $10^5\ \mathrm{s^{-1}}$; that is, the excited (I) should have rather long lifetime of $\tau \gtrsim 0.01$ ms. However, the actual lifetime of the excited (I) (^{1}CT) is much shorter than 0.01 ms; hence, the D-D scheme can also be excluded.

Reaction Mechanism of the Photoamination. The experimental results presented above exclude the reaction schemes of both A) and B-a), which was stated in the Introduction, and also Scheme C. Eventually, then, the following reaction scheme, B–b), for the mechanism of the photoamination of (I) including the CT interaction between (I) in its excited singlet state and the ground-state oxygen, comes to be the most probable one:



Reaction Scheme B-b)

In the above scheme, AQ and A denote (I) and the amine respectively. (I) in its lowest excited singlet CT state interacts with the ground-state oxygen to form the exciplex (III) (k_2). The exciplex (III) deactivates into (I) and the oxygen in the ground state (k_3) or is attacked by the amine to form the intermediate (IV) (k_4), in which a complete one-electron transfer from (I) to the oxygen molecule can occur. The deactivation (k_5), the amination (k_6), and the decomposition (k_7) take place from the intermediate (IV) at a constant ratio, along with the production of the superoxide ion, O_2^-, and the consequent formation of the peroxide. Hence, by applying the steady-state approximation for the respective intermediates, the quantum yield, Φ, of the photoamination of (I) is expressed as:

$$\Phi = C \cdot \left(\frac{k_2[\mathrm{O_2}]}{k_1 + k_2[\mathrm{O_2}]} \right) \left(\frac{k_4[\mathrm{A}]}{k_3 + k_4[\mathrm{A}]} \right) \left(\frac{k_6}{k_5 + k_6 + k_7} \right) \tag{1}$$

and the reciprocal of Φ is:

$$1/\Phi = 1/C \cdot \left(1 + \frac{k_1}{k_2[\mathrm{O_2}]} \right) \left(1 + \frac{k_3}{k_4[\mathrm{A}]} \right) \left(\frac{k_5 + k_6 + k_7}{k_6} \right) \tag{2}$$

where k_i denotes the rate constant of each process shown in the scheme and where C denotes the efficiency of the production of the aminated product (II) from the intermediate (IV). Linear relationships between $1/\Phi$ and both $1/[\mathrm{O_2}]$ and $1/[\text{amine}]$ are found in Eq. (2). If Eq. (2) is rewritten as Eq. (2′), it is obvious that the efficiency of the formation of the exciplex,

$k_2[O_2]/(k_1+k_2[O_2])$, can be given by the product of the quantum yield, Φ, and the intercept (f) in the linear plot of $1/\Phi$ against $1/[O_2]$:

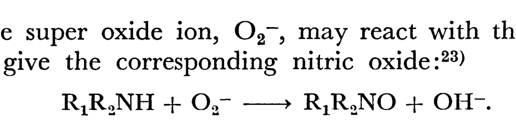
$$1/\Phi = f\cdot\left(1+\frac{k_1}{k_2[O_2]}\right) \qquad (2')$$

When ammonia (5.00×10^{-2} mol/l) was used in aerated 4 : 1 2-propanol–water, the quantum yield of the photoamination Φ was 4.8×10^{-4} and the value of the intercept in Fig. 1 was 102. Consequently, the efficiency of the exciplex (III) formation in the aerated 4 : 1 2-propanol–water mixture should be 4.9×10^{-2}; that is, the small values of the quantum yield of the photoamination of (I) are mainly ascribable to the low efficiency of the exciplex (III) formation.

Equation (2) also shows that the ratio of the intercept to the gradient in the plot of $1/\Phi$ *vs.* 1/[amine] is equal to k_4/k_3. As k_3 is the rate constant of the deactivation process of the exciplex (III) and can reasonably be assumed to be independent of the variation in the amine, the values of k_4/k_3 compared in Table 4 are proportional to the rate constant of the reaction process between the exciplex (III) and the amine. The values of k_4/k_3 of the primary amines were roughly in the order of their basicities, but the secondary amines have smaller values of k_4/k_3 than those of the primary amines. Therefore, it seems that the order of the reactivity of each amine can be explained by the basicity and steric factors and it seems reasonable that a nucleophilic attack by the amine on the exciplex (III) takes place.

The amount of the peroxide produced in the case of the alkylamines is more than ten times larger than that in the case of ammonia (Table 3). One possible explanation for this result is as follows. In the case of ammonia used as a nucleophile, the super oxide ion, O_2^-, or the peroxide may be formed in the processes giving the amination and the decomposition products from an intermediate (IV). On the other hand, in the case of alkylamines used as a nucleophile the super oxide ion, O_2^-, or the peroxide may also be formed in the deactivation process of the intermediate (IV) by an electron transfer from the alkylamine to the oxygen, since alkylamines have much lower ionization potentials than does ammonia (NH_3: I_p=10.154 eV, CH_3NH_2 : I_p=8.97 eV, $C_2H_5NH_2$: I_p=8.86 eV, and n-$C_4H_9NH_2$: I_p=8.71 eV respectively).

The fate of the superoxide ion, O_2^-, produced in the course of the reaction is considered to be as follows: hydrogen peroxide is produced by the dismutation of $HO_2\cdot$, and the hydroperoxide is also produced as:



The super oxide ion, O_2^-, may react with the amine to give the corresponding nitric oxide:[23]

$$R_1R_2NH + O_2^- \longrightarrow R_1R_2NO + OH^-.$$

Moreover, the super oxide ion, O_2^-, and $HO_2\cdot$ may participate in the decomposition process of (I) (k_7) in an oxidative manner. On the whole, the simultaneous formation of the peroxide with the photoamination can be reasonably explained, but a quantitative explanation is difficult at present.

It seems that the second molecule of (I) participates in the process after the formation of the intermediate (IV), though the role of the second molecule of (I) is not clear. The quantitative explanation of the peroxide formation and the role of the second molecule of (I) will lead to a complete elucidation of the mechanism after the formation of the intermediate (IV).

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